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96.03.27 96DE-1012032 (97.10.02) C07D 23/54, A01N 43/54, C07C 27/12, 27/24

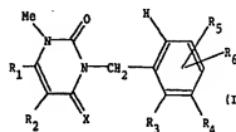
New 1-methyl-3-benzyl-6-haloalkyl-uracil derivatives - useful as pre- or post-emergence, total or selective herbicides and as defoliants or defoliants, especially for cotton (Ger)

C97-167275 NAU BG BR BY CA CN CZ GE HU IL JP KR KZ LV MX NO NZ PL RO RU SG SI SK TR UA US UZ VN R(AT BE CH DE DK EA ES FI FR GB GR IE IT LU MC NL PT SE)

Addnl. Data: MENKE O, HAMPRECHT G, HEISTRACHER E, KLINTZ R, SCHAEFER P, ZAGAR C, MENGENS M, WESTPHALEN K, WALTER H, MISSLITZ U  
97.03.10 97WO-EP01203

Substituted 1-methyl-3-benzyl-6-haloalkyl-uracil derivatives of formula (I) and their salts and enol ether derivatives are new.

C7-D12, I4-U1A, I4-VI, I4-V2, I4-V3) .3



reactant (IX)

X = O or S;

R<sub>1</sub> = -4C haloalkyl;

R<sub>2</sub> = H or halogen;

R<sub>3</sub> = H, CN, CNS, halogen, -4C haloalkyl, -4C haloalkoxy or -4C haloalkylthio;

R<sub>4</sub> = H, CNS, halogen, -4C alkyl, -4C haloalkyl, -4C alkoxy, -4C haloalkoxy, -4C haloalkylthio or alkylaminocarbonyl;

R<sub>5</sub> = (i) H, CN, NO<sub>2</sub>, OH, NH<sub>2</sub>, halogen, -4C alkylamino (optionally

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substituted by 1-4C alkyl, (1-4C)alkylcarboxyl (sic) or (1-4C)alkoxycarbonyl), haloalkoxy or haloalkylthio; or  
(ii) alkoxyl, alkylthio, cycloalkyl, cycloalkylthio, alkylenoxy, alklenethio, alkylenoxy, alkylthio, alkylcarboxyloxy, alkylcarboxylthio, alkylcarboxyloxy, alkynylcarboxyloxy, alkynylcarboxylthio, alkylsulphonyl or alkylsulphonyloxy (all optionally substituted by 1-3 of  
(a) halogen, NO<sub>2</sub>, CN, OH, cycloalkyl, alkoxyl, cycloalkoxy, alkylsulphonyl and 1-6C alkylideneamino;  
(b) phenyl, phenoxy or phenylsulphonyl (all optionally substituted by 1-3 of halogen, NO<sub>2</sub>, CN, alkyl, alkoxy and haloalkyl);  
(c) 3-7 membered heterocyclic or heterocycloxy (both optionally substituted by 1-3 of halogen, NO<sub>2</sub>, CN, alkyl, alkoxy, haloalkyl and alkylcarboxyl); and  
(d) COR<sub>1</sub>, COOR<sub>1</sub>, COSR<sub>1</sub>, CONR<sub>1</sub>R<sub>2</sub>, OCOR<sub>1</sub>, OCOOR<sub>1</sub>, OCOSR<sub>1</sub>, OCONR<sub>1</sub>R<sub>2</sub> or NR<sub>1</sub>R<sub>2</sub>);

R = H, alkyl, cycloalkyl, alkanyl, alkynyl, alkoxyalkyl, alkoxycarboxylalkyl, alkylcarboxyloxyalkyl, phenyl or phenylalkyl (where phenyl moieties are optionally substituted by 1-3 of halogen, NO<sub>2</sub>, CN, alkyl, haloalkyl, alkoxy and alkylcarboxyl);

R<sub>6</sub> = H, OH, alkyl, cycloalkyl, alkoxy, alkoxycarboxylalkoxy, alkenyl or alkenyloxy; or

NR<sub>23</sub> = 3-7 membered heterocycle (optionally substituted by 1-3 of halogen, NO<sub>2</sub>, CN, alkyl, haloalkyl, alkoxy and alkylcarboxyl);

R<sub>12</sub> = (1) OH, SH, haloalkoxy or haloalkylthio;

(2) alkoxy, alkylthio, cycloalkoxy, cycloalkylthio, alkenylthio, 5-7C cycloalkyloxy, alkylthio, alkoxythio, alkylthio, alkylcarboxyloxy, alkylcarboxylthio, alkoxycarbonyloxy, alkylcarboxyloxy, alkylcarboxylthio, alkylsulphonyl or alkylsulphonyloxy (all optionally substituted by 1-4 groups selected from groups (a)-(d) given in R<sub>3</sub> (i) (except that the Pb, PhO and PhSO<sub>2</sub> in (b) may additionally be substituted by alkoxycarbonyl), =O, =N-OR<sub>20</sub>, -C(R<sub>13</sub>)=N-OR<sub>20</sub> and SiR<sub>2</sub>R<sub>3</sub>R<sub>4</sub>); or

(3) -CYR<sub>11</sub>, -CR<sub>11</sub>(Z<sub>1</sub>R<sub>12</sub>)(Z<sub>2</sub>R<sub>13</sub>), -(C(R<sub>11</sub>))C(R<sub>14</sub>)=Q, -CHR<sub>11</sub>CHR<sub>12</sub>COOR<sub>13</sub>, COOR<sub>13</sub>, -C=CCONHOR<sub>20</sub>, -C≡CCON(R<sub>19</sub>)OR<sub>20</sub>, -C≡CCSN(R<sub>19</sub>)OR<sub>20</sub>, -C≡CC(R<sub>19</sub>)=NOR<sub>20</sub>, -NR<sub>20</sub>R<sub>3</sub>, or -C≡C-Q';

R<sub>19</sub>, R<sub>20</sub> = alkyl or 2-6C alkenyl;

Z<sub>1</sub>, Z<sub>2</sub> = O or S;

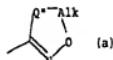
Q = CN, COR<sub>15</sub>, CH<sub>2</sub>COR<sub>15</sub>, -C(R<sub>16</sub>)=C(R<sub>17</sub>)COR<sub>15</sub>,

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CH<sub>2</sub>CHR<sub>14</sub>COR<sub>15</sub>, CONHOR<sub>20</sub>, CON(R<sub>19</sub>)OR<sub>20</sub>, CSNHOR<sub>20</sub>, CSN(R<sub>19</sub>)OR<sub>20</sub>, C(R<sub>21</sub>)=NOR<sub>20</sub> or Q';

Q' = heterocycle of formula (a);



Q' = O or S;

Alk = 1-3C alkylene (optionally substituted by alkyl);

R<sub>11</sub> = H, CN, alkyl, haloalkyl, 2-6C alkenyl, 2-6C alkynyl, cycloalkyl, alkoxyalkyl or alkoxycarbonyl;

R<sub>12</sub>, R<sub>13</sub> = alkyl, haloalkyl, alkanyl, alkynyl or alkoxyalkyl; or

R<sub>12</sub>, R<sub>13</sub> = 2-4 membered hydrocarbon chain which (i) is saturated or unsaturated, (ii) is optionally substituted by =O, (iii) optionally has one member (not adjacent to Z<sub>1</sub> or Z<sub>2</sub>) replaced by O, S or N, (iv) is optionally substituted by 1-3 of CN, NO<sub>2</sub>, NH<sub>2</sub>, halogen, 1-3C alkenyl, alkoxy, 2-6C alkenyloxy, 2-6C alkynyl, haloalkyl, cyanoalkyl, hydroxyalkyl, alkoxyalkyl,

alkenyl, alkoxyalkyl, alkynyl, alkoxyalkyl, cycloalkyl, cycloalkoxy, COOH, alkoxy carbonyl, alkylcarboxyloxyalkyl and phenyl (itself optionally substituted by 1-3 of CN, NO<sub>2</sub>, NH<sub>2</sub>, halogen, alkyl, haloalkyl, alkylthio and alkoxycarbonyl) and (v) optionally has 1 or 2 members forming part of a 3-7 membered ring (optionally containing 1 or 2 of O, S, N and N(alkyl) as heteroatom(s) and optionally substituted by 1 or 2 of CN, alkyl, 2-6C alkenyl, alkoxy, cyanoalkyl, haloalkyl and alkoxycarbonyl);

R<sub>14</sub> = H, CN, halogen, alkyl, haloalkyl, alkoxy, alkylcarboxyl or alkoxycarbonyl;

R<sub>15</sub> = H, OR<sub>22</sub>, SR<sub>22</sub>, alkyl (optionally mono- or disubstituted by alkoxy), 2-6C alkenyl, 2-6C alkynyl, haloalkyl, cycloalkyl, alkylthioalkyl, alkylaminooxy, NR<sub>23</sub>R<sub>24</sub> or phenyl (optionally substituted by 1-3 of CN, NO<sub>2</sub>, halogen, alkyl, 2-6C alkenyl, haloalkyl, alkoxy and alkoxycarbonyl);

R<sub>22</sub> = S;

R<sub>23</sub>, R<sub>24</sub> = H, alkyl, 2-6C alkenyl, 2-6C alkynyl, cycloalkyl, haloalkyl, alkoxyalkyl, alkylcarboxyl, alkoxycarbonyl, alkoxycarbonylalkyl, alkoxycarbonyl-(2-6C)alkenyl (optionally substituted in the

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(con't)

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alkenyl by 1-3 of halogen and CN), alkylsulphonyl, alkoxy carbonylalkylsulphonyl, phenyl or phenylsulphonyl (where phenyl moieties are optionally substituted by 1-3 of CN, NO<sub>2</sub>, halogen, alkyl, alkenyl, haloalkyl, alkoxy and alkoxycarbonyl); or NR<sub>31</sub>R<sub>32</sub> = 4-7 membered saturated or unsaturated heterocycle, optionally containing a second O, S, -NH or N(alkyl) heteroatom;

R<sub>15</sub> = H, CN, halogen, alkyl, alkenyl, alkynyl, alkoxyalkyl, alkylcarbonyl, alkoxycarbonyl, NR<sub>33</sub>R<sub>34</sub> or phenyl (optionally substituted by 1-3 of CN, NO<sub>2</sub>, halogen, alkyl, alkenyl, haloalkyl, alkoxy and alkoxycarbonyl);

R<sub>17</sub> = H, CN, halogen, alkyl, alkoxy, haloalkyl, alkylcarbonyl or alkoxycarbonyl;

R<sub>18</sub> = H, CN, alkyl or alkoxy carbonyl;

R<sub>19</sub> = (i) H; (ii) alkyl, haloalkyl, 2-6C alkenyl or 2-6C alkynyl (all optionally substituted by 1 or 2 of CN, halogen, OH, COOH, alkoxy, alkylthio, alkylcarbonyl, alkoxy carbonyl, alkylcarbonyloxy, alkenylcarbonyloxy and -CO-Het); (iii) alkylcarbonyl, haloalkylcarbonyl, alkoxy carbonyl, mono- or dialkylaminocarbonyl, alkoxyiminoalkyl or cycloalkyl; or (iii) phenyl or phenylalkyl (both optionally ring-substituted by 1-3 of CN, NO<sub>2</sub>, halogen, alkyl, haloalkyl, alkoxy and alkoxycarbonyl);

Het = N-bonded 3-7 membered aza-heterocycle optionally containing a second O or S heteroatom;

R<sub>20</sub> = H, alkyl, haloalkyl, cycloalkyl, alkenyl, alkynyl, hydroxalkyl, alkoxyalkyl, alkylthioalkyl, cyanoalkyl, alkylcarbonylalkyl, alkoxy carbonylalkyl, alkylcarbonyl- (2-6C) alkenyl, alkylcarbonyloxyalkyl or phenylalkyl (optionally ring-substituted by 1-3 of CN, NO<sub>2</sub>, halogen, alkyl, haloalkyl, alkoxy and alkoxycarbonyl);

R<sub>21</sub> = (i) H or halogen; (ii) alkyl, haloalkyl, alkoxy, haloalkoxy, alkylthio, alkylthio, haloalkylthio, alkylcarbonyloxy, haloalkylcarbonyloxy, alkylsulphonyloxy or haloalkylsulphonyloxy (all optionally monosubstituted by OH, CN, COOH, alkoxy, alkylthio, alkylcarbonyl, alkoxy carbonyl, mono- or dialkylaminocarbonyl or alkylcarbonyloxy); (iii)-CO-Het; (iv) alkylcarbonyl, haloalkylcarbonyl, alkoxycarbonyl, alkoxycarbonyloxy, alkylcarbonyloxy, haloalkylcarbonyloxy, alkoxycarbonyloxythio, 2-6C alkenyl, 2-6C alkenylthio, alkynyl, alkynylthio, alkylthio, (2-6C) alkynylcarbonyloxy, alkynylsulphonyloxy, cycloalkyl, cycloalkoxy, cycloalkylthio, cycloalkylcarbonyloxy or cycloalkylsulphonyloxy; or (v) phenyl, phenoxy, phenylthio, benzoyloxy, phenylsulphonyloxy,

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phenylalkyl, phenylalkoxy, phenylalkylthio, phenylalkylcarbonyloxy or phenylalkylsulphonyloxy (all optionally ring-substituted by 1-3 of CN, NO<sub>2</sub>, halogen, alkyl, haloalkyl, alkoxy and alkoxycarbonyl);

Y = O, S or NR<sub>35</sub>;

R<sub>27</sub> = (i) H, OH, alkyl, alkenyl, alkynyl, cycloalkyl, haloalkyl, alkoxalkyl, alkoxy, alkenylthio, alkylthioxy, cycloalkoxy, 5-7C cycloalkenylthio, haloalkoxy, haloalkenylthio, hydroxylalkoxy, cyanalkoxy, cycloalkylalkoxy, alkoxalkylthio, alkylalkenylthio, alkylcarbonyloxy, haloalkylcarbonyloxy, alkylcarbonyloxy, haloalkylcarbonyloxy, alkylcarbonylalkyl, alkoxycarbonylalkyl, alkylcarbonylalkoxy, alkoxycarbonylalkoxy, alkylthiobalkoxy or dialkylaminocarbonyloxy; (ii) phenyl, phenylalkoxy, phenylalkenylthio or phenylalkynylthio (all optionally ring-substituted by 1-3 of CN, NO<sub>2</sub>, halogen, alkyl, haloalkyl, 2-6 alkenyl, alkoxy and alkoxycarbonyl); and with 1 or 2 CH<sub>2</sub> units of the aliphatic chains optionally replaced by O, S or NR<sub>35</sub>; (iii) heterocyclic, heterocyclicalkyl, heterocyclicalkenylthio or heterocyclicalkynylthio (all optionally ring-substituted by 1-3 of CN, NO<sub>2</sub>, halogen, alkyl, haloalkyl, 2-6 alkenyl, alkoxy and

alkoxycarbonyl; and with 1 or 2 CH<sub>2</sub> units of the aliphatic chains optionally replaced by O, S or NR<sub>35</sub>; where heterocycles are 3-7 membered; or (iv) NR<sub>36</sub>R<sub>37</sub>;

R<sub>28</sub>R<sub>29</sub> = H, alkyl, alkenyl, alkynyl, cycloalkyl, haloalkyl, alkoxalkyl, alkylcarbonyl, alkoxycarbonylalkyl, alkoxycarbonyl, alkoxycarbonyl- (2-6C) alkenyl (optionally substituted in the alkenyl by 1-3 of halogen and CN) or phenyl (optionally substituted by 1-3 of CN, NO<sub>2</sub>, halogen, alkyl, alkenyl, haloalkyl, alkoxy and alkoxycarbonyl); or

NR<sub>36</sub>R<sub>37</sub> = 4-7 membered saturated or unsaturated heterocycle, optionally containing a further O, S, -NH or N(alkyl) heteroatom;

if R<sub>36</sub> is in the 4-position (i.e. R<sub>36</sub> is in the 5-position), then :

R<sub>36</sub> may also = (4)-CON(R<sub>31</sub>)OR<sub>32</sub>, -(CR<sub>31</sub>)<sub>2</sub>NOR<sub>32</sub>, -(C(Z<sub>1</sub>R<sub>31</sub>)Z<sub>2</sub>R<sub>32</sub>)OR<sub>33</sub>, -(C(Z<sub>1</sub>R<sub>31</sub>)(Z<sub>2</sub>R<sub>32</sub>))SR<sub>33</sub>,

(C(Z<sub>1</sub>R<sub>31</sub>)(Z<sub>2</sub>R<sub>32</sub>))NR<sub>33</sub>, Q', COOR<sub>31</sub>, COSR<sub>32</sub>, CONR<sub>31</sub>R<sub>32</sub>, alkylthio alkylcarbonyl or alkyliminoxy carbonyl;

unless specified otherwise alkyl moieties have 1-6C and alkenyl, alkynyl and cycloalkyl moieties have 3-6C.

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Enamine ester and enamine carboxylate intermediates of formulae (III) and (IV) (see 'Preparation') are also new.

#### USE

(i) are herbicides and plant desiccants/defoliants (all claimed). They are useful (i) as total herbicides or (at lower application rates) as selective herbicides for combating grassy and other weeds in crops such as wheat, rice, maize, soya and cotton, (ii) as desiccants for drying the above-ground parts of crops such as potatoes, rape, sunflowers and soya to facilitate mechanical harvesting; (iii) for promoting abscission of fruit or (iv) for controlled defoliation of useful plants, especially cotton (claimed).

Application rate is 0.001-3.0 (preferably 0.01-1.0) kg/ha, pre- or post-emergence.

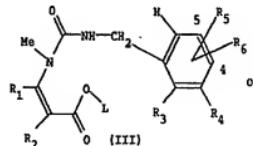
#### ADVANTAGE

(i) have stronger herbicidal activity against undesirable plants than related known compounds.

#### PREPARATION

The following processes are claimed.

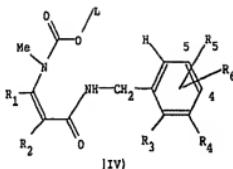
(a)



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(CON<sub>1</sub>t)

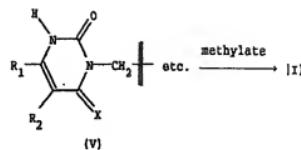
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cyclise  
base → (I; X = O)

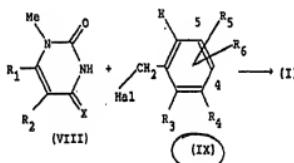
L = alkyl or phenyl.

(b)



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(c)

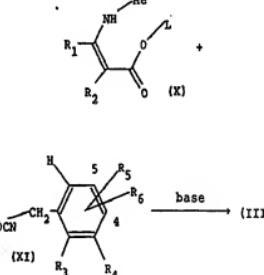


Reaction is in presence of base, or (VIII) is used in alkali metal salt form.

#### STARTING MATERIALS

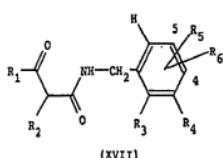
(III) and (IV) are prepared e.g. as follows.

(a)



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(b)



$\text{CH}_3\text{NHCOOL}$   
→ (IV)

#### EXAMPLE

A solution of 1.8g 3-(2,3-dichloro-4-isopropoxymethyl)-2,4-dioxo-1H-6-trifluoromethyl-1,2,3,4-tetrahydropyrimidine in 50 ml DMF was treated with 0.7g  $\text{K}_2\text{CO}_3$  and 0.7g  $\text{MgI}_2$ , stirred for 18 hrs. and treated with 150 ml ice-water. The solid product was isolated to give 1.4g of 3-(2,3-dichloro-4-isopropoxymethyl)-2,4-dioxo-1-methyl-6-trifluoromethyl-1,2,3,4-tetrahydropyrimidine (Ia), m.p. 167-168°C.

#### BIOLOGICAL ACTIVITY

(Ia) at 3.9 and 7.8 g/ha post-emergence showed good selective herbicidal activity against *Abutilon theophrasti*, *Amaranthus retroflexus* and *Solanum nigrum* in wheat. (RMH)  
(117pp2400DwgNo.0/0)  
SR-WO9504461

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